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Katsuhida MANABE et al.

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**For:** LIGHT-EMITTING SEMICONDUCTOR DEVICE GROUP III NITROGEN COMPOUND

Honorable Commissioner of Patents  
Washington, D.C. 20231

**SUBMISSION OF VERIFIED ENGLISH TRANSLATION  
OF THE PRIORITY DOCUMENT**

Sir:

Submitted herewith is a copy of the verified English translation of the Specification, Claims and Abstract, and the Declaration of Osamu Fujitani, dated December 2, 2002, that the English translation is a true English translation of the Japanese Application Number Hei-6-113484 filed on April 28, 1994, upon which application the claim for priority is based.

Approval and acknowledgment of receipt are respectfully requested.

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# DECLARATION

I, Osamu Fujitani, a Japanese citizen of Tsuchiya Bldg. 3F, 23, Ichiyanagi Dohri 1-chome, Nakagawa-ku, Nagoya-shi, Aichi-ken, 454-0905, Japan, declare that I am familiar with the Japanese and English languages, and to the best of my knowledge and belief, the attached is a full, true, and faithful English translation of the Japanese Patent Application No. Hei-6-113484 filed on April 28, 1994, made by me as a requirement for European Patent Application.



Osamu FUJITANI

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[TITLE OF THE INVENTION] LIGHT-EMITTING SEMICONDUCTOR DEVICE  
USING GROUP III NITROGEN COMPOUND

[NUMBER OF CLAIMS] 8

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[TITLE OF THE DOCUMENT] Specification

[TITLE OF THE INVENTION] LIGHT-EMITTING SEMICONDUCTOR DEVICE  
USING GROUP III NITROGEN COMPOUND

[CLAIMS]

5 [Claim 1] A light-emitting semiconductor device

comprising three layer structures of:

an n-layer with n-type conduction;

a p-layer with p-type conduction;

an emission layer which is formed therebetween with any

10 one of a homo-junction, a single hetero-junction, and a

double hetero-junction, said each of three layers being

formed with group III nitride compound semiconductor

satisfying the formula  $Al_xGa_yIn_{1-x-y}N$ , inclusive of  $x=0$ ,  $y=0$

and  $x=y=0$ ; and

15 characterized in that said emission layer is doped with

both a donor and an acceptor impurity.

[Claim 2] A light-emitting semiconductor device of claim

1, wherein said donor impurity is one of the group IV

elements and said acceptor impurity is one of the group II

20 elements.

[Claim 3] A light-emitting semiconductor device of claim

1, wherein said donor impurity is silicon (Si) and said

acceptor impurity is cadmium (Cd).

[Claim 4] A light-emitting semiconductor device of claim

25 1, wherein said donor impurity is silicon (Si) and said

acceptor impurity is zinc (Zn).

[Claim 5] A light-emitting semiconductor device of claim 1, wherein said donor impurity is silicon (Si) and said acceptor impurity is magnesium (Mg).

5 [Claim 6] A light-emitting semiconductor device of claim 1, wherein said emission layer exhibits any one of n-type conduction, semi-insulative and p-type conduction characteristics depending on concentration ratio of said donor impurity and said acceptor impurity doped thereto.

10 [Claim 7] A light-emitting semiconductor device of claim 1, wherein said donor impurity is one of the group VI elements.

[Claim 8] A light-emitting semiconductor device of claim 1, wherein the composition ratio of Al, Ga and In in said n-  
15 layer, said p-layer, which are formed on the both sides of said emission layer, and said emission layer is designed to meet each of the lattice constants of said layers to a lattice constant of a GaN n<sup>+</sup>-layer of high carrier concentration.

20 [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of the Invention]

The present invention relates to a light-emitting semiconductor device that uses a group III nitrogen compound.

25 [0002]

[Description of the Prior Art]

It has been known that an AlGaInN compound semiconductor may be used to obtain a light-emitting diode (LED) which emits blue light. This semiconductor device is  
5 useful because of its high luminous efficiency resulting from direct electron transition and because of its ability to emit blue light, which is one of the three primary colors.

[0003]

Irradiating an electron beam into an i-layer into which  
10 magnesium (Mg) is doped and heat treatment enable the i-layer to have a p-type conduction. As a result, a LED with a double hetero p-n junction structure includes an AlGaIn p-layer, a Zn-doped InGaIn emission layer and an AlGaIn n-layer, becomes useful instead of a conventional LED of MIS  
15 structure which includes an n-layer and a semi-insulating i-layer.

[0004]

[Problems to be Solved by the Invention]

The above-described LED with a double hetero p-n  
20 junction structure is doped with Zn as an emission center in the emission layer. Luminous intensity of this type of LED has been improved fairly. Still, there exists a problem in luminous efficiency and further improvement is necessary.

The emission layer of the conventional light emitting  
25 device is doped with only acceptor impurity such as



magnesium (Mg) or zinc (Zn). Therefore though the emission mechanism of the device is electron transition between conduction band and acceptor energy level, a large difference of energy levels between the conduction band and the acceptor impurity makes recombination of electrons through deep levels dominant which does not contribute to light emission. This results in lower luminous intensity. Further, the wavelength of light is about 380 to 440 nm, or shorter than that of pure blue light.

Therefore, it is an object of the present invention to solve the above problem and improve the luminous intensity of the light emitting device using AlGaInN semiconductor, and obtain enough spectrum to emit a purer blue light.

[0005]

[Means to Solve the Problems]

According to the invention of the first claim, there is provided a light-emitting semiconductor device comprising three layer structures of:

an n-layer with n-type conduction;

a p-layer with p-type conduction;

an emission layer which is formed therebetween with any one of a homo-junction, a single hetero-junction, and a double hetero-junction, said each of three layers being formed with group III nitride compound semiconductor

satisfying the formula  $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ , inclusive of  $x=0$ ,  $y=0$

and  $x=y=0$ ; and

characterized in that said emission layer is doped with both a donor and an acceptor impurity.

[0006]

5        According to the invention of the second claim, one of the group IV elements is used as the donor impurity and one of the group II elements is used as the acceptor impurity.

      According to the invention of the third claim, silicon (Si) is used as the donor impurity and cadmium (Cd) is used  
10 as the acceptor impurity.

[0007]

      According to the invention of the fourth claim, silicon (Si) is used as the donor impurity and zinc (Zn) is used as the acceptor impurity.

15        According to the invention of the fifth claim, silicon (Si) is used as the donor impurity and magnesium (Mg) is used as the acceptor impurity.

      According to the invention of the sixth claim, the emission layer can be controlled to exhibit any one of n-  
20 type conduction, semi-insulative, and p-type conduction depending on the concentration ratio of a donor impurity and an acceptor impurity doped thereto.

[0008]

      According to the invention of the seventh claim, the  
25 donor impurity can be one of the group VI elements.

According to the invention of the eighth claim, the composition ratio of Al, Ga, and In in the n-layer, the p-layer, which are formed on the both side of the emission layer, and the emission layer is designed to meet each of the lattice constants of the three layers to an n<sup>+</sup>-layer of high carrier concentration on which the three layers are formed.

[0009]

[Actions and Effects]

Doping acceptor and donor impurities into the emission layer realizes emission mechanism due to recombination of an electron at donor level and a hole at the acceptor level. This recombination also occurs within the emission layer. In result, luminous intensity is improved.

[0010]

[Examples]

Example 1

In FIG. 1 a LED 10 has a sapphire substrate 1 upon which the following five layers are consecutively formed: an AlN buffer layer 2; a silicon (Si) doped GaN n<sup>+</sup>-layer 3 of high carrier concentration; a Si-doped (Al<sub>x2</sub>Ga<sub>1-x2</sub>)<sub>y2</sub>In<sub>1-y2</sub>N n<sup>+</sup>-layer 4 of high carrier concentration; a cadmium (Cd) and Si-doped (Al<sub>x1</sub>Ga<sub>1-x1</sub>)<sub>y1</sub>In<sub>1-y1</sub>N emission layer 5; and a Mg-doped (Al<sub>x2</sub>Ga<sub>1-x2</sub>)<sub>y2</sub>In<sub>1-y2</sub>N p-layer 6. The AlN layer 2 has 500 Å thickness. The GaN n<sup>+</sup>-layer 3 is about 2.0 μm in thickness

and has a  $2 \times 10^{18}/\text{cm}^3$  electron concentration. The  $n^+$ -layer 4 is about  $2.0 \mu\text{m}$  in thickness and has a  $2 \times 10^{18}/\text{cm}^3$  electron concentration. The emission layer 5 is about  $0.5 \mu\text{m}$  in thickness. The p-layer 6 is about  $1.0 \mu\text{m}$  in thickness and has a  $2 \times 10^{17}/\text{cm}^3$  hole concentration. Nickel electrodes 7 and 8 are connected to the p-layer 6 and the  $n^+$ -layer 4, respectively. They are electrically insulated by a groove 9.

[0011]

Then, the manufacturing process of the LED 10 is described hereinafter.

The LED 10 is produced by gaseous phase growth, called metal organic vapor phase epitaxy (referred to as MOVPE hereinafter).

The gases employed in this process are ammonia ( $\text{NH}_3$ ), a carrier gas ( $\text{H}_2$  or  $\text{N}_2$ ), trimethyl gallium ( $\text{Ga}(\text{CH}_3)_3$ ) (TMG hereinafter), trimethyl aluminum ( $\text{Al}(\text{CH}_3)_3$ ) (TMA hereinafter), trimethyl indium ( $\text{In}(\text{CH}_3)_3$ ) (TMI hereinafter), dimethylcadmium ( $\text{Cd}(\text{CH}_3)_2$ ) (DMCd hereinafter), silane ( $\text{SiH}_4$ ), and biscyclopentadienyl magnesium ( $\text{Mg}(\text{C}_5\text{H}_5)_2$ ) ( $\text{CP}_2\text{Mg}$  hereinafter).

[0012]

The single crystalline sapphire substrate 1, whose main surface 'a' was cleaned by an organic washing solvent and heat treatment, was placed on a susceptor in a reaction

chamber for the MOVPE treatment. Then the sapphire substrate 1 was etched at 1100 °C by a vapor of H<sub>2</sub> fed into the chamber at a flow rate of 2 liter/min. under normal pressure.

5 [0013]

On the etched surface 'a' of the sapphire substrate 1, a 500 Å thick AlN buffer layer 2 was epitaxially formed under conditions of lowering the temperature to 400 °C, and supplying H<sub>2</sub>, NH<sub>3</sub> and TMA at a flow rate of 20 liter/min., 10 liter/min., and  $1.8 \times 10^{-5}$  mol/min., respectively. On the buffer layer 2, about a 2.2 μm thick Si-doped GaN n<sup>+</sup>-layer 3 of high carrier concentration with an electron concentration of about  $2 \times 10^{18}/\text{cm}^3$  was formed under conditions of keeping the temperature of the sapphire substrate 1 at 1150 °C.

15 [0014]

The following manufacturing process provides an active layer, or an emission layer 5, and clad layers 4 and 6; the LED 10 is designed to emit at a 430 nm wavelength peak in the luminous spectrum and have luminous centers of Cd and Si.

20 On the n<sup>+</sup>-layer 3, about a 0.5 μm thick Si-doped (Al<sub>0.47</sub>Ga<sub>0.53</sub>)<sub>0.9</sub>In<sub>0.1</sub>N n<sup>+</sup>-layer 4 of high carrier concentration with an electron concentration of  $1 \times 10^{18}/\text{cm}^3$  was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying N<sub>2</sub> or H<sub>2</sub>, NH<sub>3</sub>, TMG, TMA,

TMI, and silane at a flow rate of 10 liter/min., 10 liter/min.,  $1.12 \times 10^{-4}$  mol/min.,  $0.47 \times 10^{-4}$  mol/min., and  $0.1 \times 10^{-4}$  mol/min., respectively.

[0015]

5        On the n<sup>+</sup>-layer 4, about a 0.5  $\mu$ m thick Cd- and Si-doped  $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.94}\text{In}_{0.06}\text{N}$  emission layer 5 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying N<sub>2</sub> or H<sub>2</sub>, NH<sub>3</sub>, TMG, TMA, TMI, DMCd, and silane at a flow rate of 20 liter/min., 10  
10 liter/min.,  $1.53 \times 10^{-4}$  mol/min.,  $0.47 \times 10^{-4}$  mol/min.,  $0.02 \times 10^{-4}$  mol/min.,  $2 \times 10^{-7}$  mol/min. and  $10 \times 10^{-9}$  mol/min., respectively. At this stage, the layer 5 exhibited high resistivity. The impurity concentrations of Cd and Si doped into the emission layer 5 were  $5 \times 10^{18}/\text{cm}^3$  and  $1 \times 10^{18}/\text{cm}^3$ ,  
15 respectively.

[0016]

On the emission layer 5, about a 1.0  $\mu$ m thick Mg-doped  $(\text{Al}_{0.47}\text{Ga}_{0.53})_{0.9}\text{In}_{0.1}\text{N}$  p-layer 6 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 1100  
20 °C and supplying N<sub>2</sub> or H<sub>2</sub>, NH<sub>3</sub>, TMG, TMA, TMI, and CP<sub>2</sub>Mg at a flow rate of 20 liter/min., 10 liter/min.,  $1.12 \times 10^{-4}$  mol/min.,  $0.47 \times 10^{-4}$  mol/min.,  $0.1 \times 10^{-4}$  mol/min. and  $2 \times 10^{-4}$  mol/min., respectively. Resistivity of the p-layer 6 was  $10^8 \Omega/\text{cm}$  or more exhibiting insulative characteristics.

The impurity concentration of the Mg-doped into the p-layer 6 was  $1 \times 10^{20}/\text{cm}^3$ .

[0017]

Then, electron rays were uniformly irradiated into the p-layer 6 using a reflective electron beam diffraction device. The irradiation conditions were set at 10 KV for the accelerating voltage, 1  $\mu\text{A}$  for the sample current, 0.2 mm/sec. for the speed of the beam scanning, 60  $\mu\text{m}\phi$  for the beam aperture, and at  $5.0 \times 10^{-5}$  Torr vacuum. This irradiation changed the p-layer 6 into a p-type conductive semiconductor with a hole concentration of  $2 \times 10^{17}/\text{cm}^3$  and a resistivity of 2  $\Omega/\text{cm}$ . Thereby, a wafer with multi-structural layers was obtained as shown in FIG. 2.

[0018]

The following FIGS. 3 to 7 show sectional views of an individual element on the wafer. In actual practice and in accordance with industry custom, a wafer with a large number of elements thereon is treated by the following process and divided or diced into individual elements.

[0019]

A 2000 Å thick  $\text{SiO}_2$  layer 11 was formed on the p-layer 6 by sputtering. Then, the layer 11 was coated with a photoresist layer 12. Two selected parts or areas of the photoresist layer 12, named A and B, were removed by

photolithography as shown in FIG. 3. The part or area A is an electrode forming part which corresponds to a place where a hole 15 is formed extending to and into the  $n^+$ -layer 4 of high carrier concentration. The part or area B corresponds to a place where a groove 9 is formed for insulating or electrically insulating the part or area A from an electrode in contact with the p-layer 6.

[0020]

As shown in FIG. 4, the  $\text{SiO}_2$  layer 11 which were not covered with the photoresist layer 12 were etched off by an etching liquid such as hydrofluoric acid. Then, the exposed part of the following successive three layers from the surface of the device, the p-layer 6, the emission layer 5, and the upper part of the  $n^+$ -layer 4 of high carrier concentration, were removed by dry etching, or supplying a high-frequency power density of  $0.44 \text{ W/cm}^2$  and  $\text{BCl}_3$  gas of 10 ml/min. at a vacuum degree of 0.04 Torr as shown in FIG. 5. After that, dry etching with argon (Ar) was carried out on the device. Consequently, a hole 15 for forming an electrode reaching the  $n^+$ -layer 4 of high carrier concentration and a groove 9 for insulation are formed.

[0021]

The  $\text{SiO}_2$  layer 11 remaining on the p-layer 6 was removed by hydrofluoric acid as shown in FIG. 6. A nickel (Ni) layer 13 was laminated on the entire surface of the



device by vapor deposition. Thus, the so-formed Ni layer 13 in the hole 15 is in electrical contact with the  $n^+$ -layer 4 of high carrier concentration. A photoresist 14 was deposited on the Ni layer 13 and, then, was selectively etched off by photolithography as shown in FIG. 7 leaving patterns of configuration for electrodes connected to the  $n^+$ -layer 4 of high carrier concentration and the p-layer 6, respectively.

[0022]

Using the photoresist 14 as a mask, the exposed part or area of the Ni layer 13 from the photoresist 14 was etched off by an etching liquid such as nitric acid. At this time, the nickel layer 13 laminated in the groove 9 was also removed completely. Then, the photoresist layer 14 was removed by a photoresist removal liquid such as acetone. There were formed two electrodes, the electrode 8 for the  $n^+$ -layer 4 of high carrier concentration and the electrode 7 for the p-layer 6. A wafer treated with the above-mentioned process was divided or diced into each element which shows a gallium nitride light-emitting diode with a p-n junction structure as shown in FIG. 1.

[0023]

The obtained LED 10 was found to have a luminous intensity of 100 mcd and a wavelength of 430 nm by driving current of 20 mA.

[0024]

In order to improve luminous intensity, the preferably impurity concentration of Cd and Si doped into the emission layer 5 is in the  $1 \times 10^{17}/\text{cm}^3$  to  $1 \times 10^{20}/\text{cm}^3$  range,

5 respectively. It is further desirable that the concentration of Si is smaller than that of Cd by 1/2 to 1/10.

[0025]

In order to make the band gap of the emission layer 5  
10 smaller than those of its respective adjacent two layers, i.e., the p-layer 6 and the  $n^+$ -layer 4 of high carrier concentration, a double hetero-junction structure was utilized for the LED 10 in this embodiment.

Further, it is preferable that the composition ratio of  
15 Al, Ga, and In in the respective three layers 4, 5, and 6 is selectively designed to meet the lattice constants of their layers 4, 5, and 6 with the lattice constant of GaN in the  $n^+$ -layer 3 of high carrier concentration, a double hetero-junction structure was utilized for the LED 10 in this  
20 embodiment.

Further, it is preferable that the composition ratio of Al, Ga, and In in the respective three layers 4, 5, and 6 is selectively designed to meet the lattice constants of their layers 4, 5, and 6 with the lattice constant of GaN in the  
25  $n^+$ -layer 3 of high carrier concentration as precisely as

possible.

Alternatively, a single hetero-junction structure can be utilized.

[0026]

5     Example 2

The emission layer 5 in Example 1 was doped with cadmium (Cd) and silicon (Si). In this Example 2, an emission layer 5 is doped with Zn and Si as shown in FIG. 8. After forming the  $n^+$ -layers 3 described above, about a 0.5  
10    $\mu\text{m}$  thick Si-doped  $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.94}\text{In}_{0.06}\text{N}$   $n^+$ -layer 4 of high carrier concentration with an electron concentration of  $2 \times 10^{19}/\text{cm}^3$  was formed on the  $n^+$ -layer 3 under conditions of keeping the temperature of the sapphire substrate constant at 800 °C, and supplying  $\text{N}_2$ ,  $\text{NH}_3$ , TMG, TMA, TMI, and silane  
15   at a flow rate of 20 liter/min., 10 liter/min.,  $1.12 \times 10^{-4}$  mol/min.,  $0.47 \times 10^{-4}$  mol/min., and  $0.1 \times 10^{-4}$  mol/min., respectively.

[0027]

About a 0.5  $\mu\text{m}$  thick Si- and Zn-doped  
20    $(\text{Al}_{0.09}\text{Ga}_{0.91})_{0.99}\text{In}_{0.01}\text{N}$  emission layer 5 was formed under conditions of keeping the temperature constant at 1150 °C, and supplying  $\text{N}_2$ ,  $\text{NH}_3$ , TMG, TMA, TMI, silane, and DEZ for 7 min. at a flow rate of 20 liter/min., 10 liter/min.,  $1.53 \times 10^{-4}$  mol/min.,  $0.47 \times 10^{-4}$  mol/min.,  $0.02 \times 10^{-4}$  mol/min. and

10 x 10<sup>-9</sup> mol/min., and 2 x 10<sup>-4</sup> mol/min., respectively. The impurity concentration of Zn and Si doped into the emission layer 5 was 2 x 10<sup>18</sup>/cm<sup>3</sup> and 1 x 10<sup>18</sup>/cm<sup>3</sup>, respectively.

[0028]

5 About a 1.0 μm thick Mg-doped (Al<sub>0.3</sub>Ga<sub>0.7</sub>)<sub>0.94</sub>In<sub>0.06</sub>N p-layer 6 was formed under conditions of keeping the temperature constant at 1100 °C, and supplying N<sub>2</sub>, NH<sub>3</sub>, TMG, TMA, TMI, and CP<sub>2</sub>Mg at a flow rate of 20 liter/min., 10 liter/min., 1.12 x 10<sup>-4</sup> mol/min., 0.47 x 10<sup>-4</sup> mol/min., 0.1 x 10<sup>-4</sup> mol/min., and 2 x 10<sup>-4</sup> mol/min., respectively. The impurity concentration of Mg doped into the p-layer 6 was 1 x 10<sup>20</sup>/cm<sup>3</sup>. At this stage, the p-layer 6 remained insulative with a resistivity of 10<sup>8</sup> Ω<sup>1</sup>/<sub>4</sub>cm or more.

[0029]

15 Then, the p-layer 6 was processed to have p-type conduction by electron beam irradiation under the same conditions that described in Example 1. The subsequent process steps are the same as that described in the previous example. The so-obtained LED 10 was found to have a  
20 luminous intensity of 1000 mcd and a wavelength of 430 nm.

[0030]

### Example 3

FIG. 9 shows a structural view of a LED embodied in Example 3. The LED in Example 3 was manufactured by

additionally doping Mg into the emission layer 5 of the LED in Example 2. Other layers except for the emission layer 5 were manufactured in the same way as those described in Example 2.

5 CP<sub>2</sub>Mg was fed at a flow rate of  $2 \times 10^{-4}$  mol/min. into a chamber in addition to the gasses employed in Example 2 in order to manufacture the emission layer 5 in Example 3.

[0031]

10 The emission layer 5 was about 0.5  $\mu\text{m}$  thick comprising Mg, Zn, and Si-doped  $(\text{Al}_{0.09}\text{Ga}_{0.91})_{0.99}\text{In}_{0.01}\text{N}$ . Its resistivity was  $10^8 \Omega\text{cm}$  remaining insulative. Impurity concentration of Mg, Zn, and Si was  $1 \times 10^{19}/\text{cm}^3$ ,  $2 \times 10^{18}/\text{cm}^3$ , and  $1 \times 10^{18}/\text{cm}^3$ , respectively.

[0032]

15 Then, both of the emission layer 5 and a p-layer 6 were subject to electron beam irradiation with the electron beam diffraction device under as same conditions as that described in Example 1. Thus, the emission layer 5 and the p-layer 6 became exhibiting p-type conduction with a hole  
20 concentration of  $2 \times 10^{17}/\text{cm}^3$  and resistivity of  $2 \Omega\text{cm}$ .

[0033]

#### Example 4

The LED embodied in Example 4 has a single hetero-junction structure and an emission layer 5 made of GaN.

Namely, one junction is made of a heavily Si-doped  $n^+$ -layer 4 of high carrier concentration and a Zn- and Si-doped GaN emission layer 5, and the other junction is the GaN emission layer 5 and a Mg-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  p-layer 61 with p-type conduction. In this example, the Mg-doped GaN p-layer 62 as a contact layer is formed on the p-layer 61. A groove 9 for insulating separation is formed through the contact layer 62, the p-layer 61 and the emission layer 5.

[0034]

10 As shown in FIG. 10, the LED 10 has a sapphire substrate 1 upon which the following five layers are consecutively formed: an AlN buffer layer 2; a Si-doped GaN  $n^+$ -layer 4 of high carrier concentration; a Zn and Si-doped GaN emission layer 5, Mg-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  p-layer 61, and Mg-doped GaN contact layer 62. The AlN layer 2 has a 500 Å thickness. The GaN  $n^+$ -layer 4 has about a 4.0  $\mu\text{m}$  thickness and a  $2 \times 10^{18}/\text{cm}^3$  electron concentration. The emission layer 5 has about a 0.5  $\mu\text{m}$  thickness. The p-layer 61 has about a 0.5  $\mu\text{m}$  thickness and a  $2 \times 10^{17}/\text{cm}^3$  hole concentration. The contact layer 62 has about a 0.5  $\mu\text{m}$  thickness and a  $2 \times 10^{17}/\text{cm}^3$  hole concentration. Nickel electrodes 7 and 8 are formed to connect the contact layer 62 and the  $n^+$ -layer 4 of high carrier concentration, respectively. The two electrodes are electrically insulated

by a groove 9.

[0035]

Here is explained a manufacturing process of the LED 10.  
The sapphire substrate 1 and the AlN buffer layer 2 were  
5 prepared by the same process that described in detail in  
Example 1. On the AlN buffer layer 2, about a 4.0  $\mu\text{m}$  thick  
Si-doped GaN  $n^+$ -layer 4 of high carrier concentration with  
an electron concentration of  $2 \times 10^{18}/\text{cm}^3$  was formed under  
conditions of keeping the temperature of sapphire substrate  
10 1 constant at 1150  $^{\circ}\text{C}$ .

[0036]

The manufacturing process condition and composition  
ratio of the three layers, the emission layer 5 as an active  
layer, the p-layer 62 as a clad layer, and the contact layer  
15 62 are described hereinafter to set the wavelength at 430 nm  
at peak in the luminous spectrum by using luminous centers  
of Zn and Si. After the  $n^+$ -layer 4 of high carrier  
concentration was formed, about a 0.5  $\mu\text{m}$  thick Zn- and Si-  
doped GaN emission layer 5 was formed under conditions of  
20 keeping the temperature of the sapphire substrate 1 at 1000  
 $^{\circ}\text{C}$  and supplying  $\text{N}_2$  or  $\text{H}_2$ ,  $\text{NH}_3$ , TMG, DMZ, and silane at a  
flow rate of 20 liter/min., 10 liter/min.,  $1.53 \times 10^{-4}$   
mol/min.,  $2 \times 10^{-7}$  mol/min.,  $10 \times 10^{-9}$  mol/min., respectively.

[0037]

About a 0.5  $\mu\text{m}$  thick Mg-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  p-layer 61 was formed under conditions of keeping the temperature at 1000  $^{\circ}\text{C}$ , and supplying  $\text{N}_2$  or  $\text{H}_2$ ,  $\text{NH}_3$ , TMG, TMA, and  $\text{CP}_2\text{Mg}$  for 7 min. at a flow rate of 20 liter/min., 10 liter/min.,  $1.12 \times 10^{-4}$  mol/min.,  $0.47 \times 10^{-4}$  mol/min., and  $2 \times 10^{-7}$  mol/min., respectively. At this stage, the p-layer 61 remained insulative with a resistivity of  $10^8 \Omega/\text{cm}$  or more. The impurity concentration of Mg doped into the p-layer 61 was  $1 \times 10^{19}/\text{cm}^3$ .

[0038]

Then, about a 0.5  $\mu\text{m}$  thick Mg-doped GaN contact layer 62 was formed under conditions of keeping the temperature at 1000  $^{\circ}\text{C}$ , and supplying  $\text{N}_2$  or  $\text{H}_2$ ,  $\text{NH}_3$ , TMG, and  $\text{CP}_2\text{Mg}$  at a flow rate of 20 liter/min., 10 liter/min.,  $1.12 \times 10^{-4}$  mol/min., and  $2 \times 10^{-4}$  mol/min., respectively. At this stage, the Mg-doped contact layer 62 remained insulative with a resistivity of  $10^8 \Omega/\text{cm}$  or more. The impurity concentration of Mg doped into the contact layer 62 was  $1 \times 10^{20}/\text{cm}^3$ .

[0039]

Then, the p-layer and contact layer 62 were uniformly irradiated by an electron beam under the same conditions as described in Example 1. Consequently, the p-layer 61 and contact layer 62 were processed to exhibit p-type conduction with a  $2 \times 10^{17}/\text{cm}^3$  hole concentration and  $2 \Omega/\text{cm}$  resistivity.



[0040]

As a result, the LED 10 having a single hetero-junction structure was obtained whose emission layer was doped with Zn as an acceptor and Si as a donor impurity. Alternatively, doping Mg and irradiating electrons into the emission layer 5 can be used to obtain an emission layer 5 with p-type conduction.

[0041]

Example 5

The following points are different from the Example 4. As shown in FIG. 11 the emission layer 5 is made of Zn- and Si-doped  $\text{Al}_{x_2}\text{Ga}_{1-x_2}\text{N}$ . The p-layer 61 is made of Mg-doped  $\text{Al}_{x_1}\text{Ga}_{1-x_1}\text{N}$ . The  $n^+$ -layer 4 of high carrier concentration is made of Si-doped  $\text{Al}_{x_3}\text{Ga}_{1-x_3}\text{N}$ . The composition ratio of  $x_1$ ,  $x_2$  and  $x_3$  in each layer is designed to make the band gap of the emission layer 5 smaller than those of the  $n^+$ -layer 4 and p-layer 61 forming a double hetero-junction structure or a single hetero-junction structure. Thanks to this structure, carriers are confined in the emission layer 5 contributing to higher luminous intensity.

The emission layer 5 can exhibit any one of semi-insulative, p-type conductivity, or n-type conductivity.

[0042]

Example 6

The following points are different from the Example 5.

As shown in FIG. 12 the emission layer 5 is made of Zn- and Si-doped  $\text{Ga}_y\text{In}_{1-y}\text{N}$ . The p-layer 61 is made of Mg-doped  $\text{Al}_{x_1}\text{Ga}_{1-x_1}\text{N}$ . The  $n^+$ -layer 4 of high carrier concentration is made of Si-doped  $\text{Al}_{x_2}\text{Ga}_{1-x_2}\text{N}$ . The composition ratio of  $x_1$ ,  $y$ , and  $x_2$  in the respective p-layer 61, the emission layer 5, and the  $n^+$ -layer 4 is designed to make the band gap of the emission layer 5 smaller than those of the  $n^+$ -layer 4 and the p-layer 61 forming a double hetero-junction structure or a single hetero-junction structure. Thanks to this structure, carriers are confined in the emission layer 5 contributing to higher luminous intensity.

The emission layer 5 can exhibit any one of semi-insulative, p-type conductivity, or n-type conductivity.

[0043]

As shown in FIG. 13, the LED 10 in this example has a sapphire substrate 1 which has the following five layers consecutively formed thereon: an AlN buffer layer 2; a Si-doped GaN  $n^+$ -layer 4 of high carrier concentration; a Zn- and Si-doped  $\text{Ga}_{0.94}\text{In}_{0.06}\text{N}$  emission layer 5, an Mg-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  p-layer 61, and an Mg-doped GaN contact layer 62. The AlN layer 2 has a 500 Å thickness. The GaN  $n^+$ -layer 4 has about a 4.0  $\mu\text{m}$  thickness and a  $2 \times 10^{18}/\text{cm}^3$  electron concentration. The emission layer 5 has about 0.5  $\mu\text{m}$  thickness. The p-layer 61 has about a 0.5  $\mu\text{m}$  thickness and

a  $2 \times 10^{17}/\text{cm}^3$  hole concentration. The contact layer 62 has about a  $0.5 \mu\text{m}$  thickness and a  $2 \times 10^{17}/\text{cm}^3$  hole concentration. Nickel electrodes 7 and 8 are formed to connect to the contact layer 62 and the  $n^+$ -layer 4 of high carrier concentration, respectively. The two electrodes are electrically insulated by a groove 9.

[0044]

A manufacturing process for the LED 10 is described hereinafter. The sapphire substrate 1 and the AlN buffer layer 2 were prepared by the same process that described in detail in Example 1. About a  $4.0 \mu\text{m}$  thick Si-doped GaN  $n^+$ -layer 4 of high carrier concentration with an electron concentration of  $2 \times 10^{18}/\text{cm}^3$  was formed under conditions of keeping the temperature of the sapphire substrate 1 at  $1150^\circ\text{C}$ .

[0045]

Following manufacturing process and composition ratio for the three layers, the emission layer 5 as an active layer, the p-layer 61 as a clad layer, and the contact layer 62, show an example where the LED 10 is designed to have 450 nm wavelength at peak in luminous spectrum and have luminous centers of Zn and Si. After forming the above-described  $n^+$ -layer 4 of high carrier concentration, about a  $0.5 \mu\text{m}$  thick Zn- and Si-doped  $\text{Ga}_{0.94}\text{In}_{0.06}\text{N}$  emission layer 5 was formed on

the n<sup>+</sup>-layer 4 under conditions of keeping the temperature at 850 °C, and supplying N<sub>2</sub> or H<sub>2</sub>, NH<sub>3</sub>, TMG, TMI, DMZ and, silane at a flow rate of 20 liter/min., 10 liter/min., 1.53 x 10<sup>-4</sup> mol/min., 0.02 x 10<sup>-4</sup> mol/min., 2 x 10<sup>-7</sup> mol/min., and 5 10 x 10<sup>-9</sup> mol/min., respectively.

[0046]

About a 0.5 μm thick Mg-doped Al<sub>0.1</sub>Ga<sub>0.9</sub>N p-layer 61 was formed on the emission layer 5 under conditions of keeping the temperature at 850 °C, and supplying N<sub>2</sub> or H<sub>2</sub>, NH<sub>3</sub>, TMG, 10 TMA, and CP<sub>2</sub>Mg for 7 min. at a flow rate of 20 liter/min., 10 liter/min., 1.12 x 10<sup>-4</sup> mol/min., 0.47 x 10<sup>-4</sup> mol/min., and 2 x 10<sup>-7</sup> mol/min., respectively. At this stage, the p-layer 61 remained insulative with a resistivity of 10<sup>8</sup> Ω<sub>sq</sub>/cm or more. The impurity concentration of Mg doped into the p- 15 layer 61 was 1 x 10<sup>19</sup>/cm<sup>3</sup>.

[0047]

Then, about a 0.5 μm thick Mg-doped GaN contact layer 62 was formed under conditions of keeping the temperature at 850 °C and supplying N<sub>2</sub> or H<sub>2</sub>, NH<sub>3</sub>, TMG, and CP<sub>2</sub>Mg at a flow 20 rate of 20 liter/min., 10 liter/min., 1.12 x 10<sup>-4</sup> mol/min., and 2 x 10<sup>-4</sup> mol/min., respectively. The impurity concentration of the Mg doped into the contact layer 62 was 1 x 10<sup>20</sup>/cm<sup>3</sup>. At this stage, the Mg-doped contact layer 62 remained insulative with a resistivity of 10<sup>8</sup> Ω<sub>sq</sub>/cm or more.

[0048]

Then, the p-layer 61 and the contact layer 62 were uniformly irradiated by an electron beam with the same conditions that described in Example 1. Consequently, the p-layer 61 and the contact layer 62 were processed to exhibit p-type conduction with a  $2 \times 10^{17}/\text{cm}^3$  hole concentration and a  $2 \Omega\text{cm}$  resistivity.

[0049]

In Examples 1 to 6, the emission layer 5 can exhibit any one of semi-insulation, p-type conductivity, or n-type conductivity.

In order to improve the luminous intensity, the impurity concentration of Zn and Si doped into the emission layer 5 is preferable in the  $1 \times 10^{17}/\text{cm}^3$  to  $1 \times 10^{20}/\text{cm}^3$  range, respectively. The concentration is more preferable in the  $1 \times 10^{18}/\text{cm}^3$  to  $1 \times 10^{19}/\text{cm}^3$  range. It is not preferable that the impurity concentration be lower than  $1 \times 10^{18}/\text{cm}^3$ , because the luminous intensity of the LED decreases as a result. It is not desirable that the impurity concentration is higher than  $1 \times 10^{19}/\text{cm}^3$ , because poor crystallinity occurs. It is preferable that the concentration of Si is 0.1 to 10 times as same as that of Zn. The most preferable concentration of Si is 0.1 to 1 times as same as that of Zn or lesser than that of Zn.

[0050]

Further, the emission layer 5 exhibits semi-insulative i-type characteristic when concentration of doped Cd is higher than that of doped Si. The emission layer 5 exhibits n-type conduction when concentration of doped Cd is smaller than that of doped Si.

[0051]

In the embodiments, cadmium (Cd) was used as an acceptor impurity and silicon (Si) as a donor impurity. Alternatively, beryllium (Be), magnesium (Mg), zinc (Zn), cadmium (Cd) and mercury (Hg) can be used as an acceptor impurity. Alternatively, carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) can be used as a donor impurity.

[0052]

Further alternatively, sulfur (S), selenium (Se), and tellurium (Te) can be used as a donor impurity. Electron irradiation was used in order to get p-type conduction. Alternatively, annealing, heat processing in the atmosphere of N<sub>2</sub> plasma gas and laser irradiation can be used.

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a diagram showing the structure of the LED embodied in Example 1;

FIG. 2 is a sectional view illustrating a step of producing the LED embodied in Example 1;

FIG. 3 is a sectional view illustrating a step of

producing the LED embodied in Example 1;

FIG. 4 is a sectional view illustrating a step of producing the LED embodied in Example 1;

FIG. 5 is a sectional view illustrating a step of producing the LED embodied in Example 1;

FIG. 6 is a sectional view illustrating a step of producing the LED embodied in Example 1;

FIG. 7 is a sectional view illustrating a step of producing the LED embodied in Example 1;

FIG. 8 is a diagram showing the structure of the LED embodied in Example 2;

FIG. 9 is a diagram showing the structure of the LED embodied in Example 3;

FIG. 10 is a diagram showing the structure of the LED embodied in Example 4;

FIG. 11 is a diagram showing the structure of the LED embodied in Example 5;

FIG. 12 is a diagram showing the structure of the LED embodied in Example 6; and

FIG. 13 is a diagram showing the structure of the LED embodied in Example 6.

[Reference Characters]

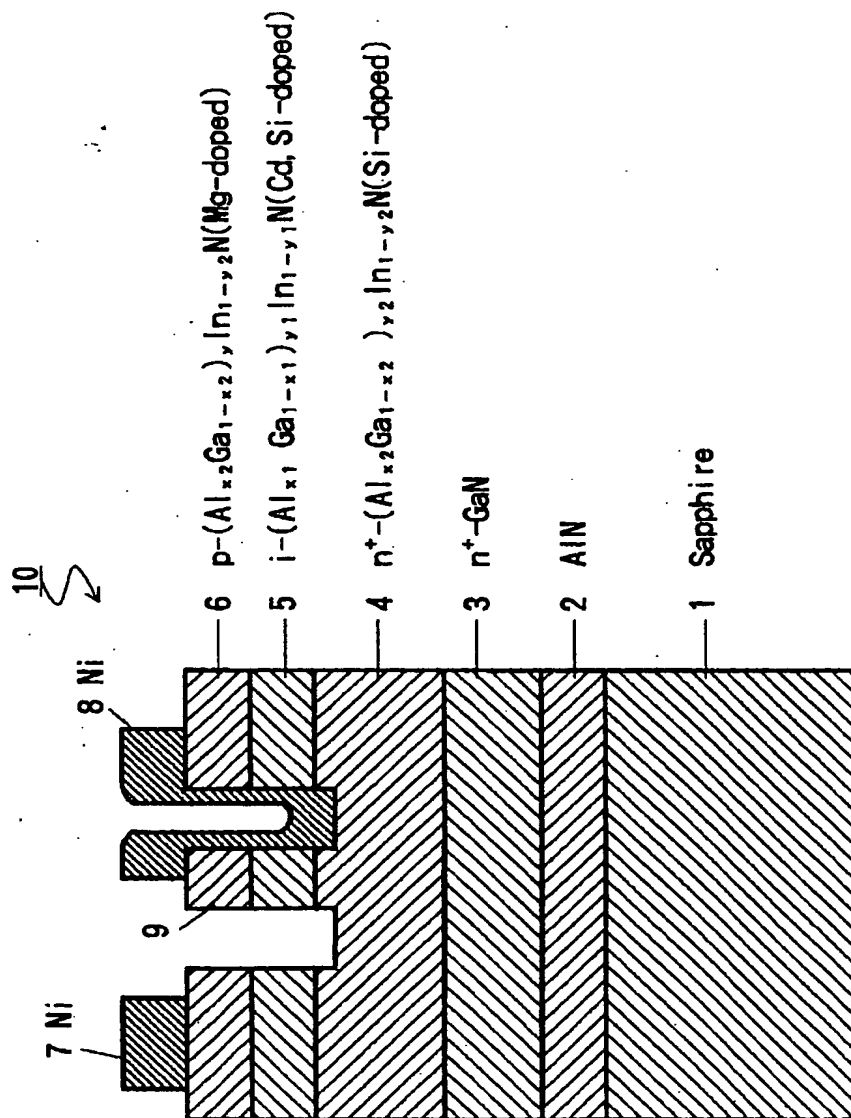
10...light-emitting diode

1...sapphire substrate

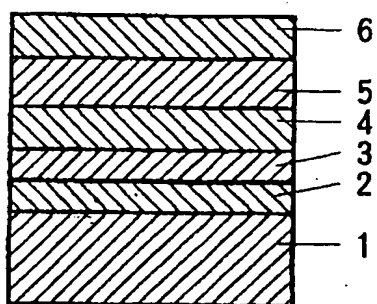
25 2...buffer layer

- 3...n<sup>+</sup>-layer of high carrier concentration
- 4...n<sup>+</sup>-layer of high carrier concentration
- 5...emission layer
- 6...p-layer
- 5 61...p-layer
- 62...cap layer
- 7, 8...electrodes
- 9...groove

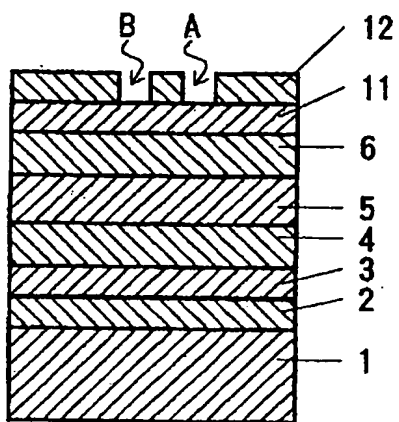




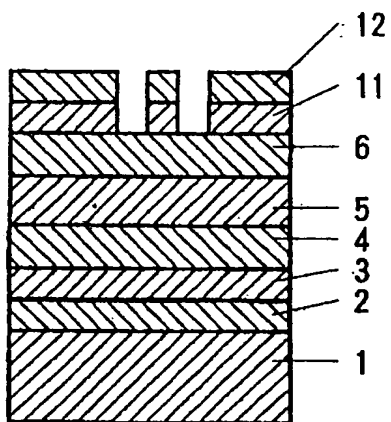
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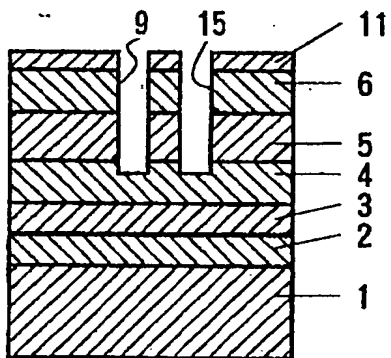
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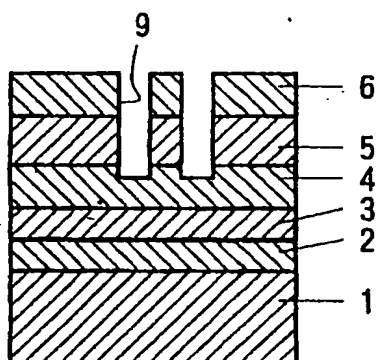
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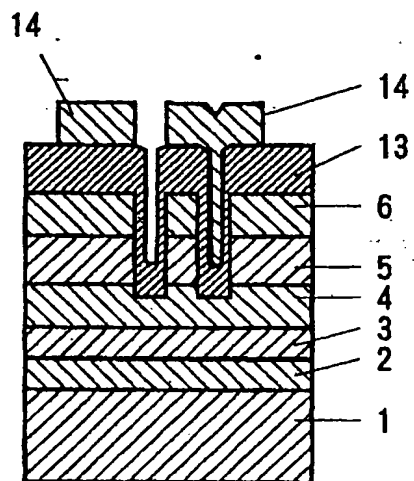
【 F I G . 5 】



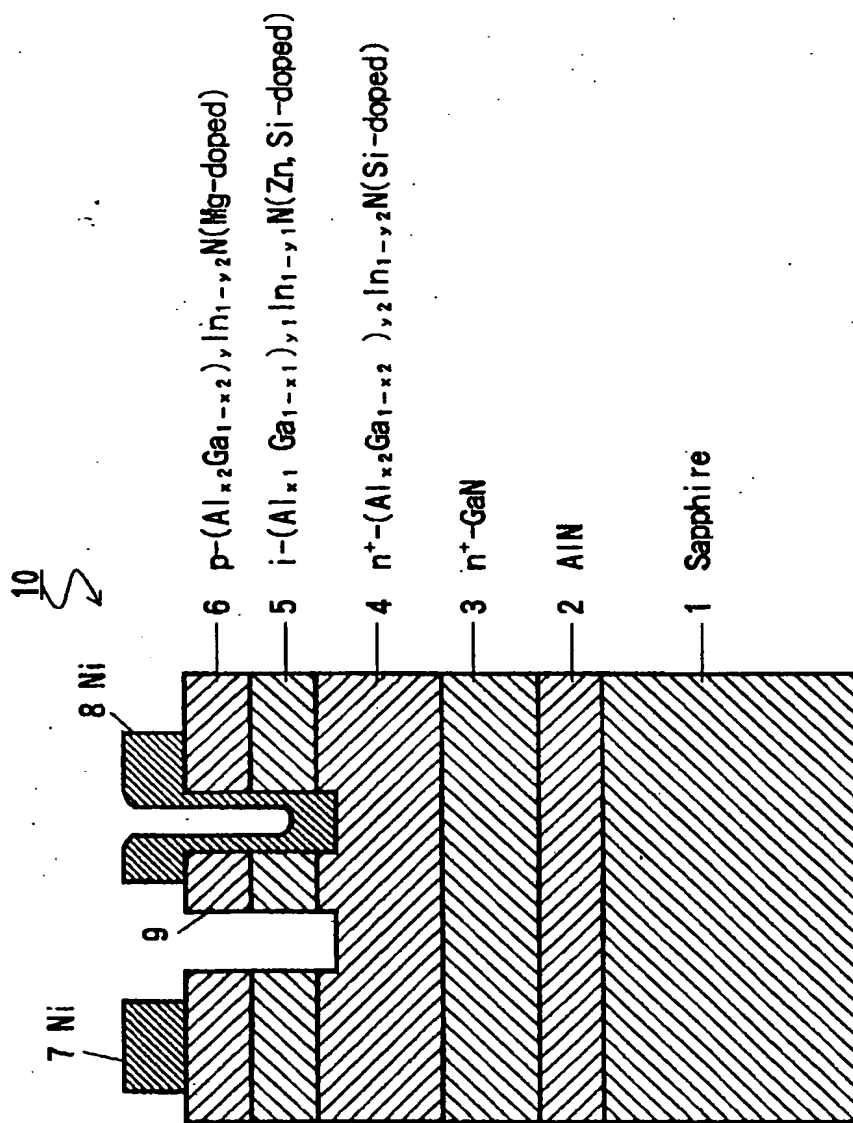
【 F I G . 6 】



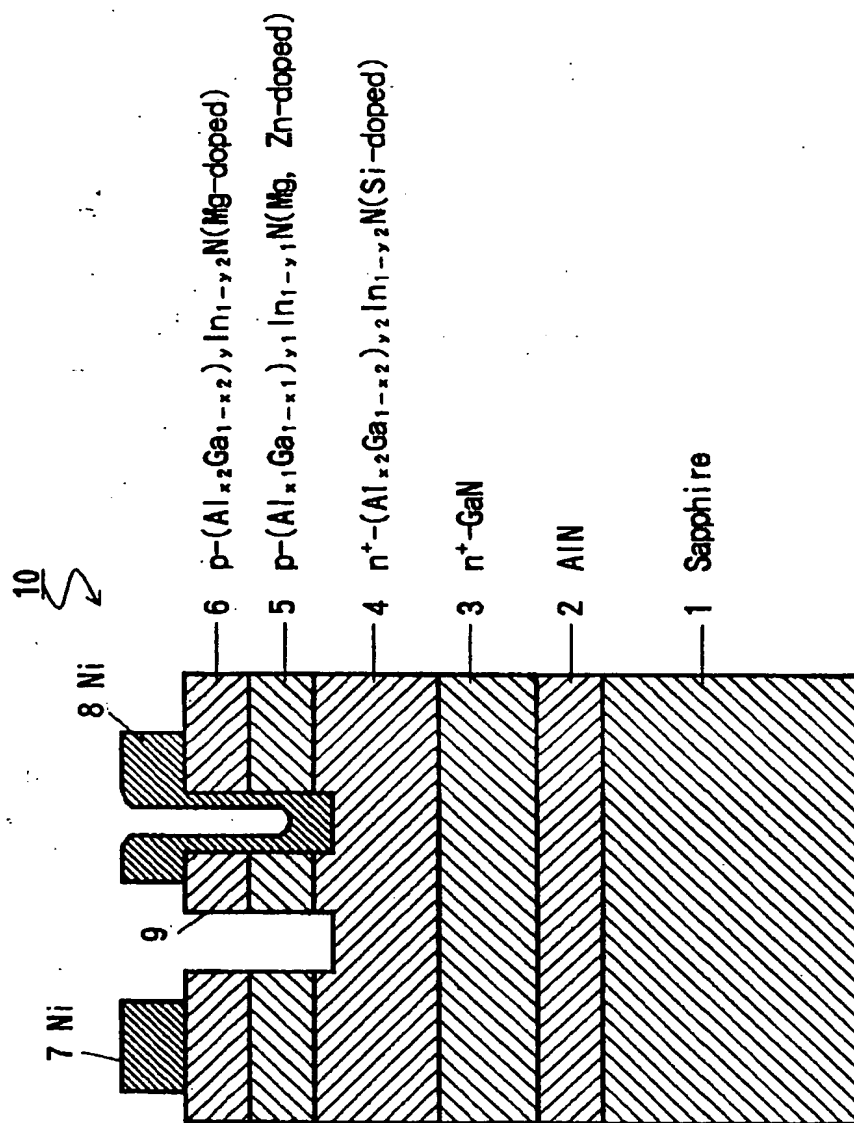
【 F I G . 7 】



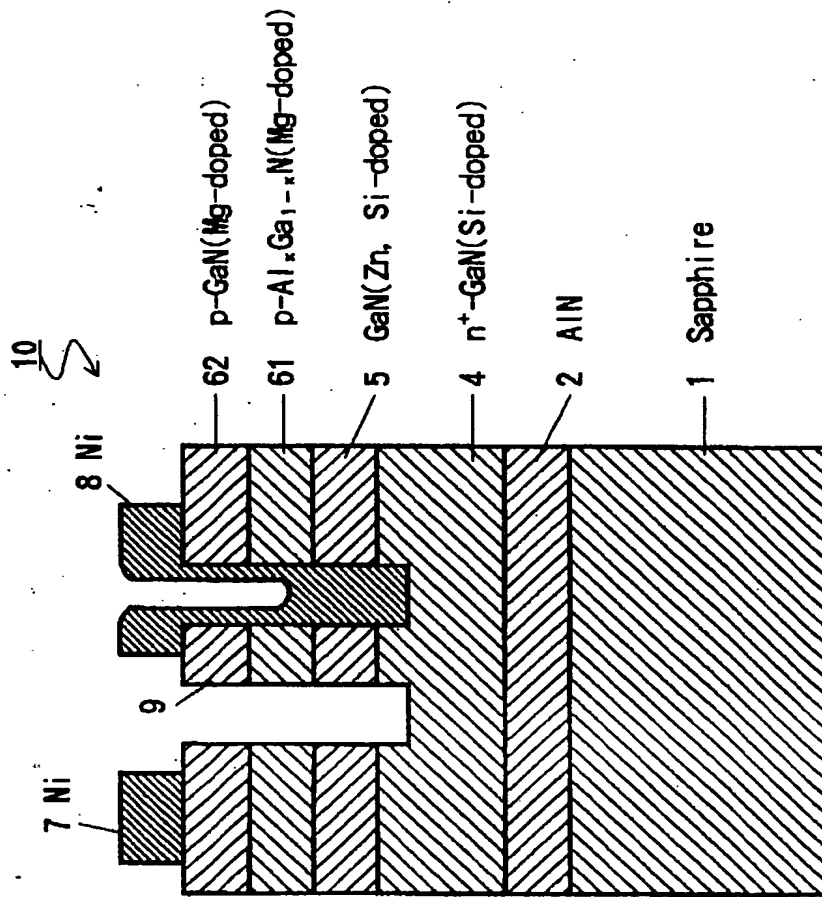
【 F I G . 8 】



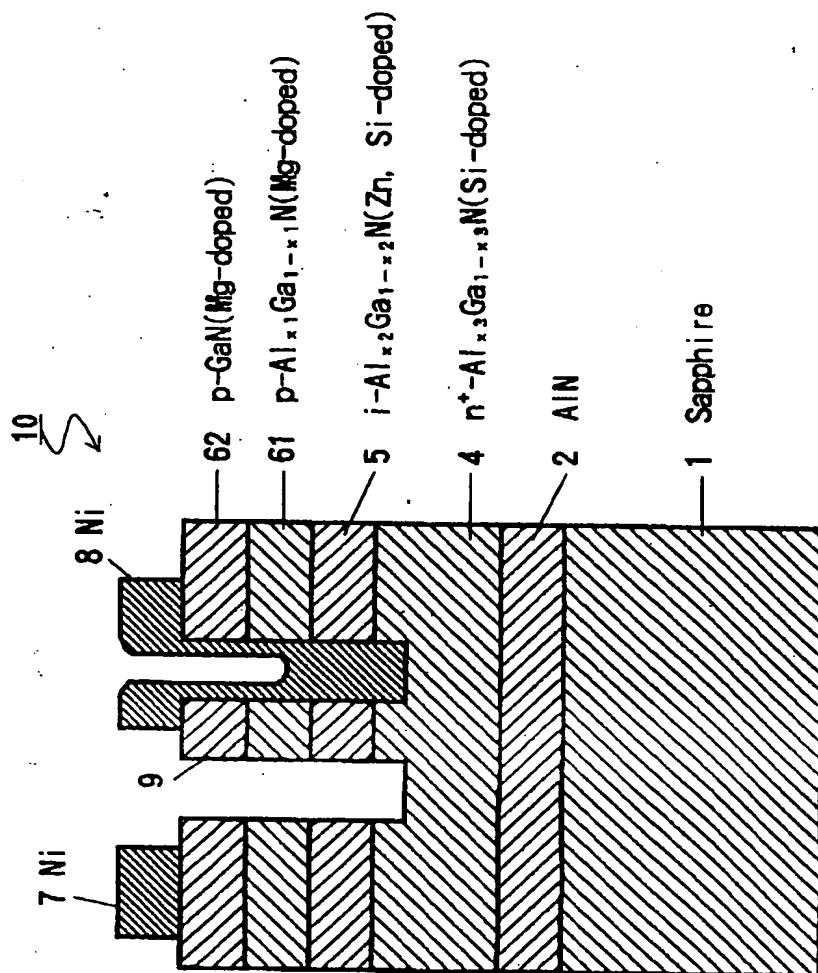
【 FIG. 9 】



【 FIG. 10 】

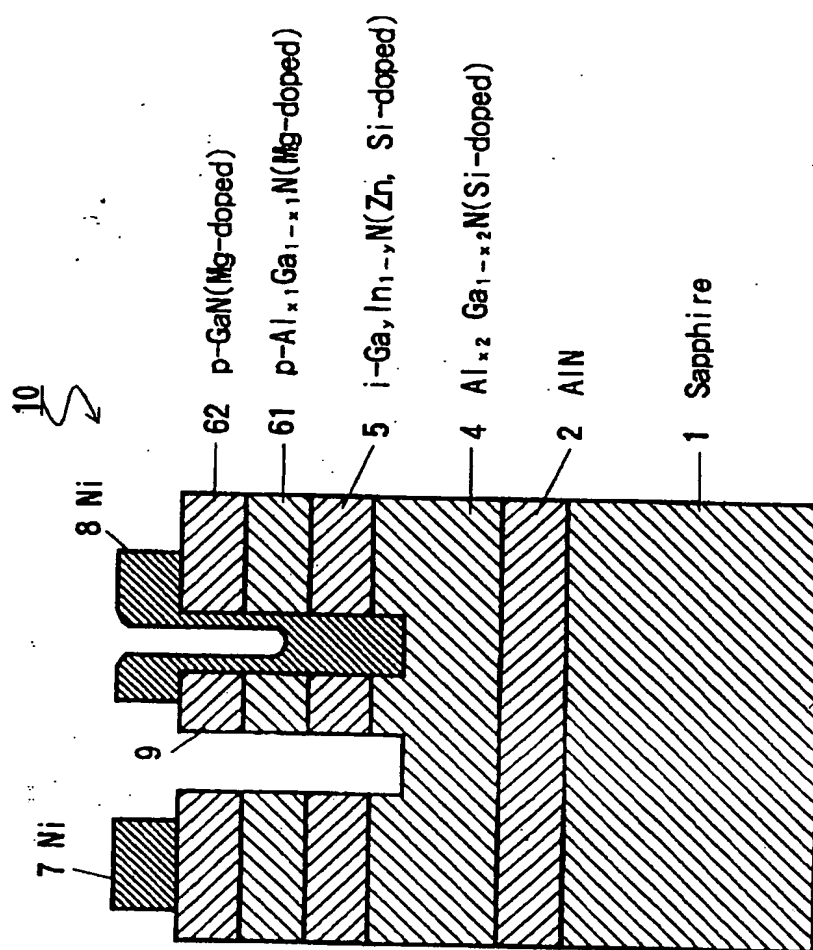


【 FIG. 11 】

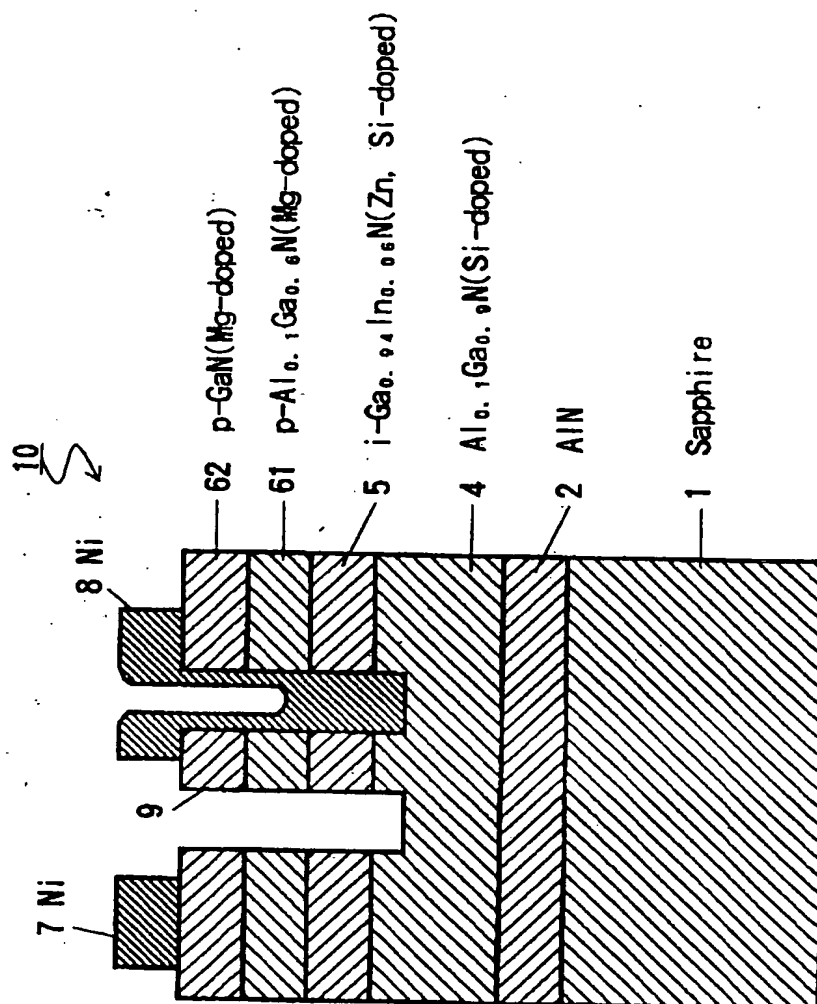




【 FIG. 12 】



【FIG. 13】



[TITLE OF THE DOCUMENT] Abstract

[OBJECT] To improve luminous intensity and to obtain purer blue color.

[CONSTITUTION] An AlN buffer layer 2 with thickness of 500 Å is formed on a sapphire substrate 1. A silicon (Si) doped GaN n<sup>+</sup>-layer 3 of high carrier concentration, a Si-doped (Al<sub>x2</sub>Ga<sub>1-x2</sub>)<sub>y2</sub>In<sub>1-y2</sub>N n<sup>+</sup>-layer 4 of high carrier concentration, a zinc (Zn) and Si-doped (Al<sub>x1</sub>Ga<sub>1-x1</sub>)<sub>y1</sub>In<sub>1-y1</sub>N emission layer 5, and a Mg-doped (Al<sub>x2</sub>Ga<sub>1-x2</sub>)<sub>y2</sub>In<sub>1-y2</sub>N p-layer 6 are successively formed. The GaN n<sup>+</sup>-layer 3 has about a 2.0 μm thickness and a 2 x 10<sup>18</sup>/cm<sup>3</sup> electron concentration. The n<sup>+</sup>-layer 4 has about a 2.0 μm thickness and a 2 x 10<sup>18</sup>/cm<sup>3</sup> electron concentration. The emission layer 5 has about a 0.5 μm thickness. The p-layer 6 has about a 1.0 μm thickness and a 2 x 10<sup>17</sup>/cm<sup>3</sup> hole concentration. Nickel electrodes 7 and 8 are connected to the p-layer 6 and the n<sup>+</sup>-layer 4, respectively. A groove 9 electrically insulates the electrodes 7 and 8. The composition ratio of Al, Ga, and In in each of the layers 4, 5, and 6 is selected to meet the lattice constant of the n<sup>+</sup>-layer 3.

[SELECTED FIGURE] FIG. 1